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ELLIPSOMETRIC STUDY OF OXIDE FILMS FORMED ON LDEF METAL SAMPLES

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ABSTRACT

The optical constants of samples of six different metals (Al, Cu, Ni, Ta, W, and Zr) exposed to space on the long duration exposure facility (LDEF) have been studied by variable angle spectroscopic ellipsometry. Measurements were also carried out on portions of each sample which were shielded from direct exposure by a metal bar. A least-squares fit of the data using an effective medium approximation was then carried out with thickness and composition of surface films formed on the metal substrates as variable parameters. The analysis revealed that exposed portions of the Cu, Ni, Ta, and Zr samples are covered with porous oxide films ranging in thickness from 500 Å to 1000 Å. The 410 Å thick film of Al_2O_3 on the exposed Al sample is practically free of voids. Except for Cu, the shielded portions of these metals are covered by thin nonporous oxide films characteristic of exposure to air. The shielded part of the Cu sample has a much thicker porous coating of Cu_2O. The tungsten data could not be analyzed.

CONTENTS

SYMBOLS

subscript p:		polarization parallel to plane of incidence (horizontal plane)
subscript s:		polarization perpendicular (senkrecht) relative to plane of incidence
subscript i:		incident wave
subscript r:		reflective wave
L	=	skin depth
E	=	oscillating electric vector (complex)
r_p	=	E_{pr} / E_{pi}
r_s	=	E_{sr} / E_{si}
n	=	index of refraction
k	=	extinction coefficient
$\tan \psi$	=	amplitude ratio = $\lvert r_p / r_s \rvert$
Δ	=	phase difference between the p-polarized and s-polarized components of the reflected light
ϕ	=	angle of incidence
λ	=	wavelength in Angstroms
Å	=	Angstrom = 10^{-8} cm

INTRODUCTION

The technique of characterizing surface films and multilayer materials by spectroscopic ellipsometry has been greatly advanced in the last thirty years.[1-6] In this technique, a plane-polarized monochromatic collimated light beam is reflected from the surface being analyzed. The reflected light will then be elliptically polarized. In order to determine the parameters of the ellipse a Fourier analysis is performed of the time-varying intensity of the reflected beam after transmission through a rotating analyzer.

The important ellipsometric parameters ψ and Δ are derived from the real part of tan ψ cos Δ and the imaginary part tan ψ sin Δ of the complex reflectivity ratio:

$$r_p / r_s = e^{i\Delta} \tan \psi. \tag{1}$$

The optical constants n (index of refraction) and k (extinction coefficient) are computed from ψ and Δ. For a layered structure the values of n and k so obtained are pseudo-optical constants; i.e., not related to the optical properties of a single substance.

The values of ψ and Δ measured in this fashion reflect the composition of the surface to a depth on the order of the skin depth, L; a quantity that depends upon the conductivity of the surface material at optical frequencies. For metals of high conductivity (e.g., aluminum) L is less than 200 Å for visible light; however, for metals of low conductivity like tungsten L is substantially larger. For semiconductors like Cu_2O or CuO, L is still larger, and for transparent insulators like Al_2O_3 or ZrO_2 L is effectively infinite.

EXPERIMENTAL

Square plates of dimensions 0.3 x 5 x 5 cm^3 of the six metals Al, Cu, Ni, Ta, W, and Zr were mounted on the long duration exposure facility (LDEF) in the locations indicated in Table 1 and then examined by ellipsometry after recovery. An aluminum bar 0.63 cm wide was affixed across the middle of each plate and shielded a portion of each sample from direct exposure to the space environment, as shown in Figure 1.

Table 1. LOCATION OF SAMPLES ON SATELLITE

Sample	Tray	Location
Aluminum	D3	Trailing Edge
Copper	G12	Earth End
Nickel	D3	Trailing Edge
Tantalum	D9	Leading Edge
Tungsten	D9	Leading Edge
Zirconium	D9	Leading Edge

1. BUDDE, W. *Photoelectric Analysis of Polarized Light.* Applied Optics, v. 1, 1962, p. 201-205.
2. GREEF, R. *An Automatic Ellipsometer for Use in Electrochemical Investigations.* Rev. Scient. Inst., v. 41, 1970, p. 532-538.
3. SUITS, J. C. *Magneto-Optical Rotation and Ellipticity Measurements with a Spinning Analyzer.* Rev. Scient. Inst., v. 42, 1971, p. 19-22.
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5. BU-ABBUD, G. H, BASHARA, N. M., and WOOLLAM, J. A. *Variable Wavelength, Variable Angle Ellipsometry.* Thin Solid Film, v. 138, 1986, p. 27-41.
6. WOOLLAM, J. A., SNYDER, P. O., and ROST, M. C. *Variable Angle Spectroscopic Ellipsometry: A Non-Destructive Characterization Technique for Ultra-Thin and Multilayer Materials.* Thin Solid Films, v. 166, 1988, p. 317-323.

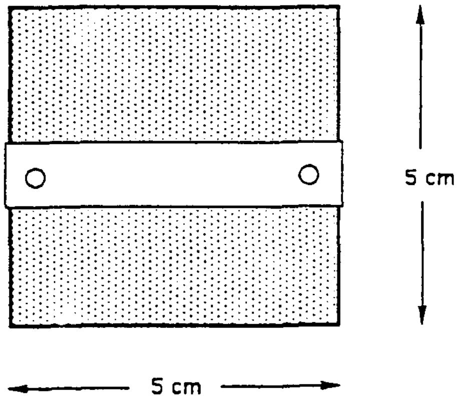

Figure 1. Diagram of metal plate with shielding strap.

A schematic diagram of the ellipsometer used to obtain the optical data is shown in Figure 2. White light is generated from a high pressure xenon arc lamp and passes successively through a step-motor-controlled grating monochromator, an electronically controlled shutter, and a linear polarizer before reflection from the surface of the sample. The reflected light is directed through a rotating analyzer before falling on the photocathode of a photomultiplier.

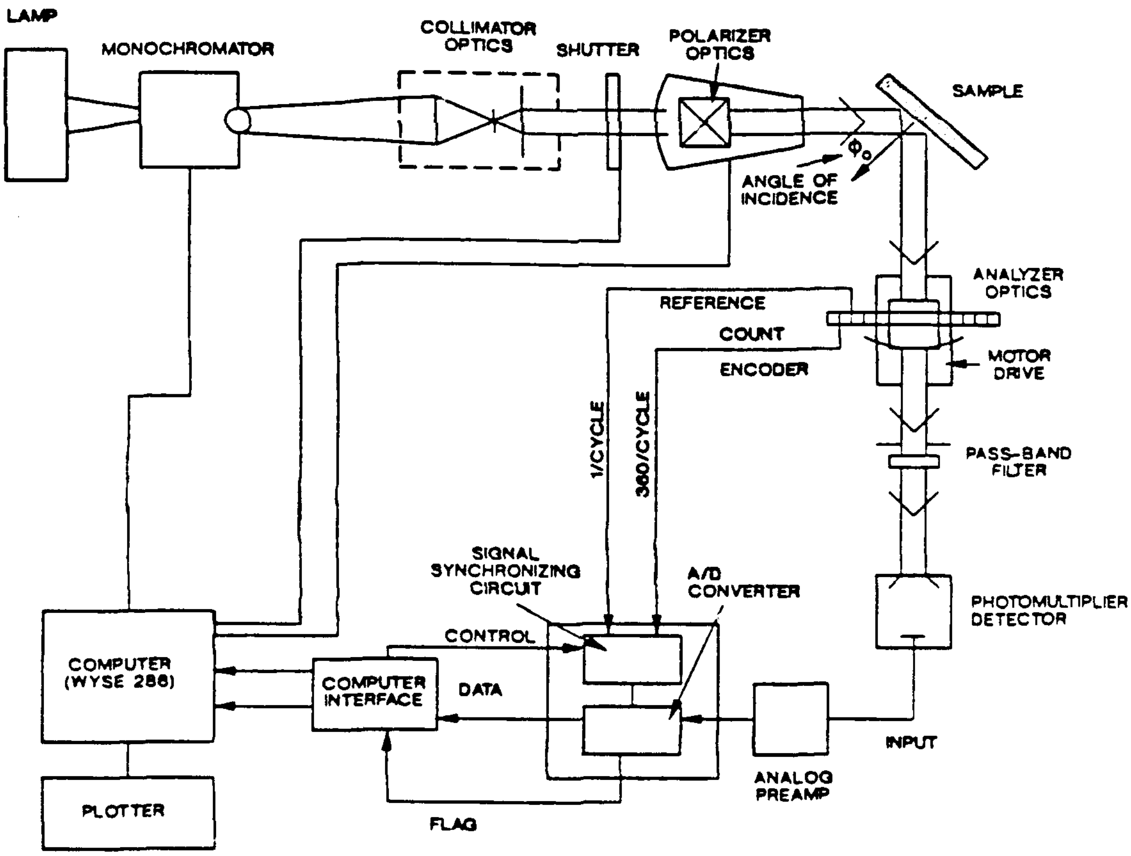

Figure 2. Schematic diagram of variable angle ellipsometer; designed and built by the J.A. Woolam Company, Lincoln, Nebraska.

During an experimental run at a fixed angle of incidence ϕ data is obtained after executing a data acquisition program with input for ϕ, polarizer setting, wavelength range, and sampling increment. For a given wavelength setting λ the program subtracts the output of the multiplier for 150 revolutions of the analyzer with the shutter open from a similar output obtained with the shutter closed. This effectively eliminates any contribution from background radiation. The step-motor is computer-driven to advance the wavelength setting of the monochromator to the next programmed sampling point and the procedure just described is repeated. Most of the data reported herein was recorded over a wavelength range from 4000 Å to 8000 Å in 200 Å steps, and each set of data was obtained at three different angles of incidence for each specimen.

A computer program analyzes the output of the photomultiplier in terms of the Fourier coefficients of the time-varying optical signal and derives the corresponding values of the ellipsometric angles ψ and Δ for each wavelength setting. The measured values of ψ and Δ are functions of the change in the polarization of the reflected light from the sample and with mathematical manipulation can yield a great deal of information about surface structure and composition. For this purpose a software package (VASE) written by J. A. Woollam Company was employed. VASE uses the Marquardt algorithm and a Bruggeman Effective Medium Approximation[6] to make a least-squares fit of a model of the surface variable parameters to the experimental data. Every material represented in our model must have a table of optical constants available in the same wavelength range as for the experimental data.

For the LDEF samples a model was chosen consisting of a metal substrate covered by a porous oxide film. The porosity of the film was defined by the proportion of voids (air) present in it. That proportion and the thickness of the film were the two variable parameters in the least-squares fitting procedure. Published data obtained for each oxide-free metal substrate, bulk measurements for the appropriate metal oxide, and optical constants for air was used to fit the model.

RESULTS

Aluminum

The Al_2O_3 film formed on aluminum when exposed to air is usually 20 Å to 55 Å thick.[7] The difficulty of producing a smooth optically flat surface on metallic aluminum is well known.[8] A critical selection from among the large number of studies of the optical constants of aluminum has been made by D. Y Smith, et al.[9] For amorphous Al_2O_3 data obtained by Hageman, et al.[10] was used.

A good fit was obtained for the exposed part of the sample for a 395 Å thick film of Al_2O_3 containing no voids which covers a metallic aluminum substrate. The shielded portion consists of a 68 Å thick layer of Al_2O_3 over metallic aluminum. The data obtained on the aluminum sample are shown in Figures 3 and 4.

7. HALFORD, J., CHIN, F. K., and NEWMAN, J. E. *Effects of Vacuum Deposition Conditions on Ellipsometric Parameters, Optical Constants, and Reflectance of Ultrapure Aluminum Films.* Journ. Opt. Soc. Am., v. 63, 1973, p. 786-792.
8. NATISHAN, P. M., PEACE, G. T., and SLEBODNIK, P. F. *Surface Preparation of Aluminum for Ion Implantation.* Metallography, v. 23, 1989, p. 21-26.
9. SMITH, D. Y., SHILES, E., and INOKUTI, M. The Optical Properties of Metallic Aluminum. Handbook of Optical Constants Solids, E. Palik, ed., 1985, p. 398-399.
10. HAGEMAN, H. J., GUDAR, W., and KUNZ, C. *Optical Constants from the Far Infrared to the X-Ray Region: Mg, Al, Cu, Ag, Au, Bi, C, and Al_2O_3.* Journ. Opt. Soc. Am., v. 65, 1975, p. 742-745.

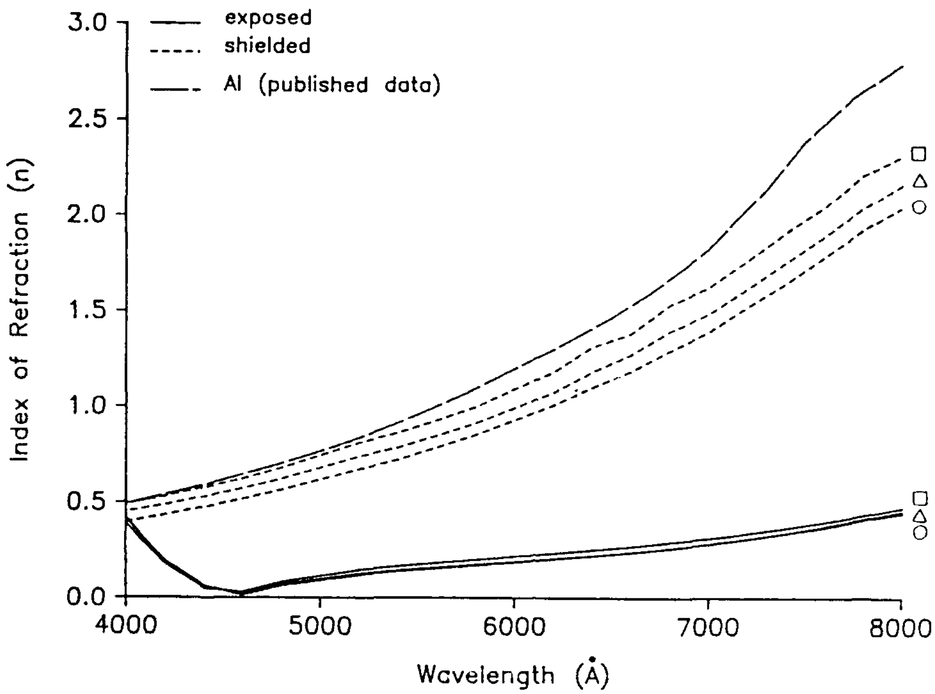

Figure 3. Index of refraction of LDEF aluminum sample for exposed region and shielded region. Index of refraction of aluminum (Reference 9). □ ≡ angle of incidence = ϕ = 65°; Δ ≡ ϕ = 70°; o ≡ ϕ = 75°.

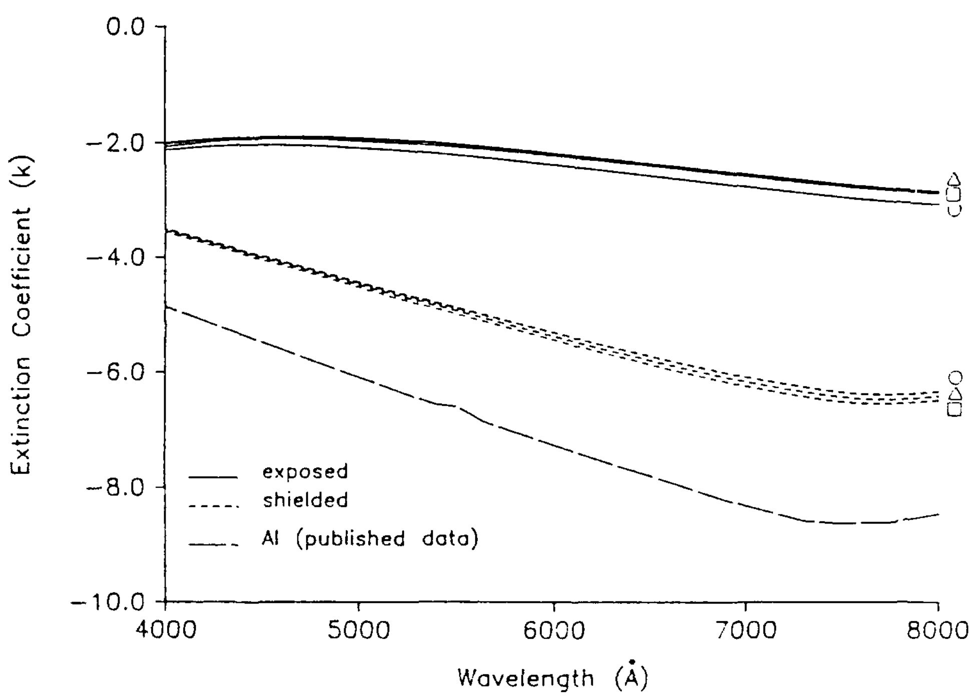

Figure 4. Extinction coefficient of LDEF aluminum sample for exposed region and shielded region. Extinction coefficient of refraction of aluminum (Reference 9). □ ≡ angle of incidence = ϕ = 65°; Δ ≡ ϕ = 70°; o ≡ ϕ = 75°.

Copper

Many measurements of the optical constants of copper have been reported in the literature; the choice used was made by D. Y. Lynch and W. R. Hunter.[11] There are two stoichiometric copper oxides; cuprous oxide Cu_2O (red), and cupric oxide CuO (black). The copper-oxygen phase diagram shows a strong pressure dependence that causes CuO to be transformed into Cu_2O in a high vacuum[12] and, therefore, also presumably in space. A selection from among various values of the optical constants of both oxides has been made by C.G. Ribbing and A. Roos.[12]

The exposed portion of the copper sample fits a model consisting of a very thick (1039 Å) porous layer of Cu_2O containing 71% voids over metallic copper. The unexposed portion can be modelled by a 449 Å thick film of Cu_2O containing 69% voids over the metal. The optical constants for the exposed and shielded regions of the copper sample are shown in Figures 5 and 6. The results of the least-squares best fit for the exposed portion of this sample are shown in Figures 7 and 8.

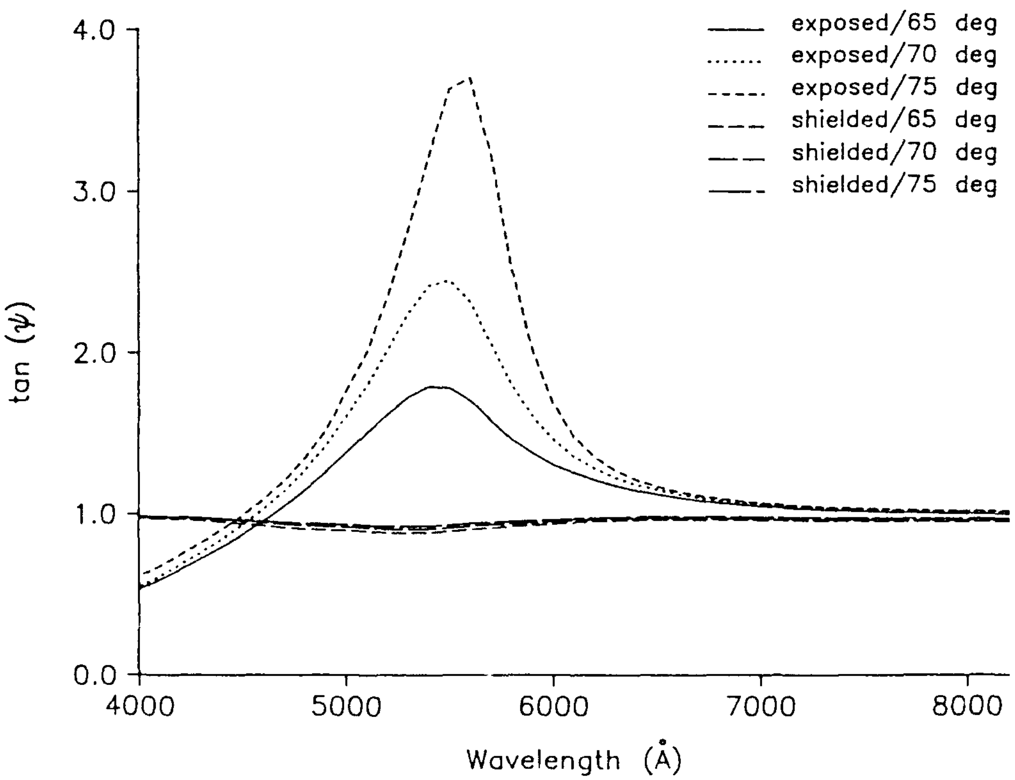

Figure 5. Tan ψ of LDEF copper sample for exposed region and shielded region.

11. LYNCH, D. W., and HUNTER, W. R. Optical Constants of Metals. Handbook of Optical Constants of Solids, E. Palik, ed., 1985, p. 280-285.
12. RIBBING, C. G., and ROOS, A. Copper Oxides (Cu_2O, CuO). Handbook of Optical Constants of Solids II, E. Palik, ed., 1991, p. 875-882.

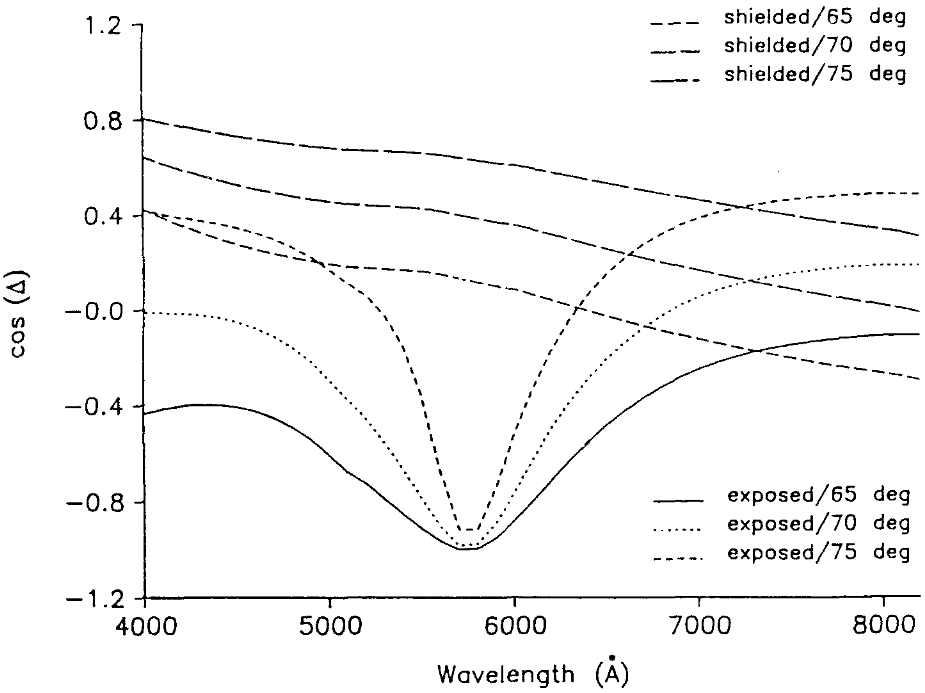

Figure 6. Cos Δ of LDEF copper sample for exposed region and shielded region.

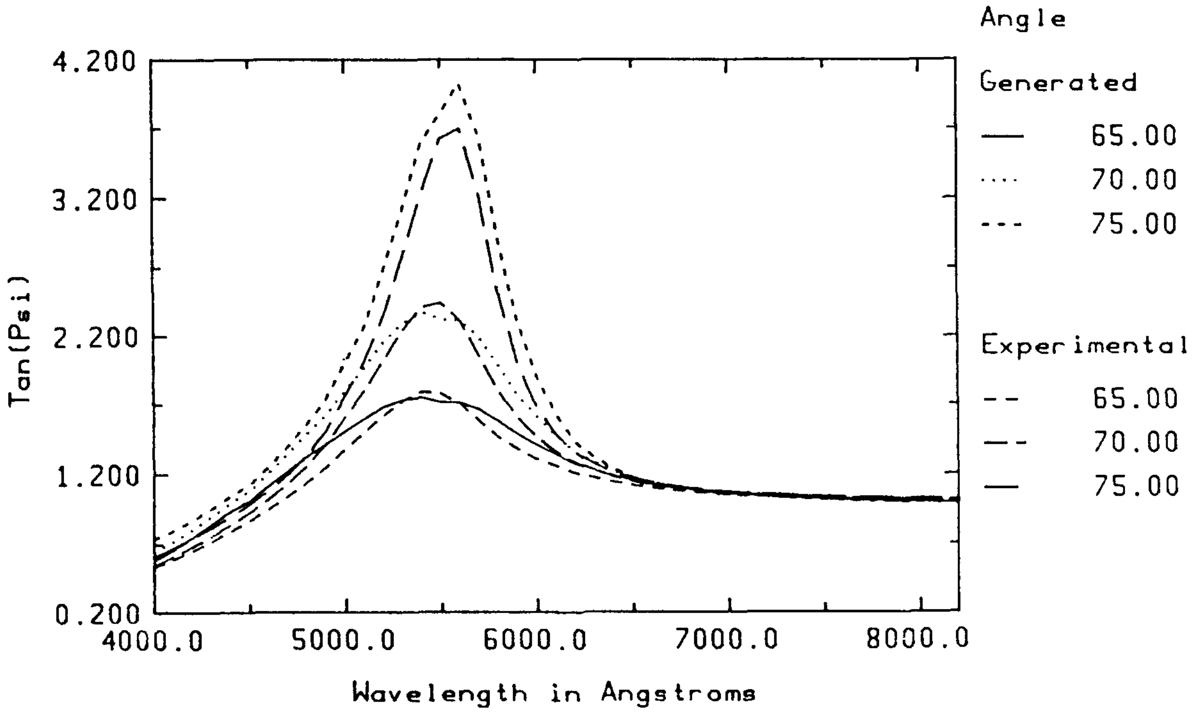

Figure 7. Experimental data shows tan ψ for the LDEF copper sample (exposed region); the generated data are obtained for the model of a 1039 Å thick film Cu_2O containing 71% voids on metallic copper.

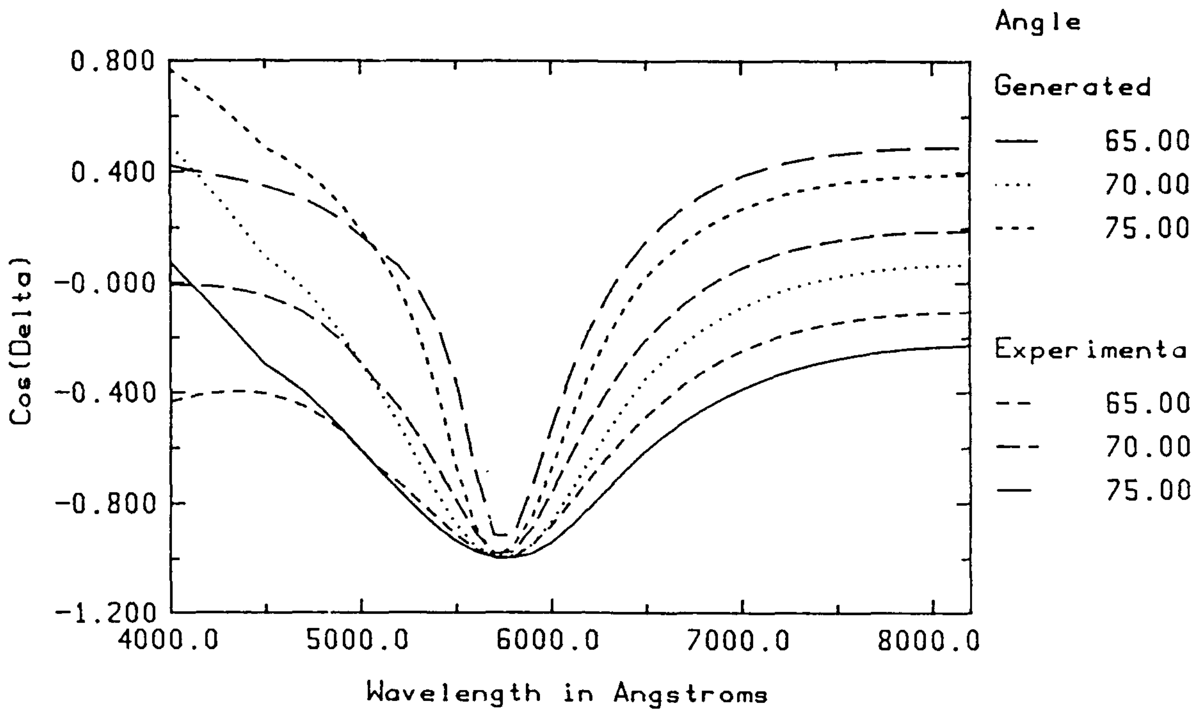

Figure 8. Experimental data shows cos Δ for the LDEF copper sample (exposed region); the generated data are obtained for the model of a 1039 Å thick film of Cu_2O containing 71% voids on metallic copper.

Nickel

To construct models for the nickel sample, values of the optical constants reported by P. B. Johnson and R. W. Christy[13] were used for the metal, but for NiO only a few scattered values in the literature[14] were found. For that reason, our own measurements were made on a polished crystal of NiO provided by Professor Clive Perry of Northeastern University. The results of this experiment are listed in Table 2. For the exposed region on the nickel sample, the measured optical constants fit a model that consists of a porous 687 Å thick layer of NiO containing 65% voids over metallic nickel. The best fit for the shielded region converges to a value of 60 Å for the thickness of the oxide layer, with no voids present, over metallic nickel. Plots of the data for the Ni sample are shown in Figures 9 and 10.

13. JOHNSON, P. B., and CHRISTY, R. W. *Optical Constants of the Transition Metals: Ti, V, Cr, Mn, Fe, Co, Ni, and Pd.* Phys. Rev., v. B9, 1974, p. 5056-5070.

14. LANDOLT-BÖRNSTEIN. Zahlenwerte und Funktionen, v. II, part 8, 1962, p. 2-198.

Table 2. MEASURED OPTICAL CONSTANTS OF NICKEL OXIDE

Wavelength (Å)	Index of Refraction	Extinction Coefficient
4000	1.929	0.483
4200	1.901	0.499
4400	1.888	0.520
4600	1.879	0.534
4800	1.882	0.550
5200	1.890	0.586
5400	1.901	0.604
5600	1.904	0.622
5800	1.919	0.642
6000	1.932	0.660
6200	1.938	0.676
6400	1.952	0.693
6600	1.965	0.709
6800	1.978	0.725
7000	1.987	0.740
7200	2.002	0.759
7400	2.026	0.777
7600	2.041	0.790
7800	2.048	0.801
8000	2.065	0.813

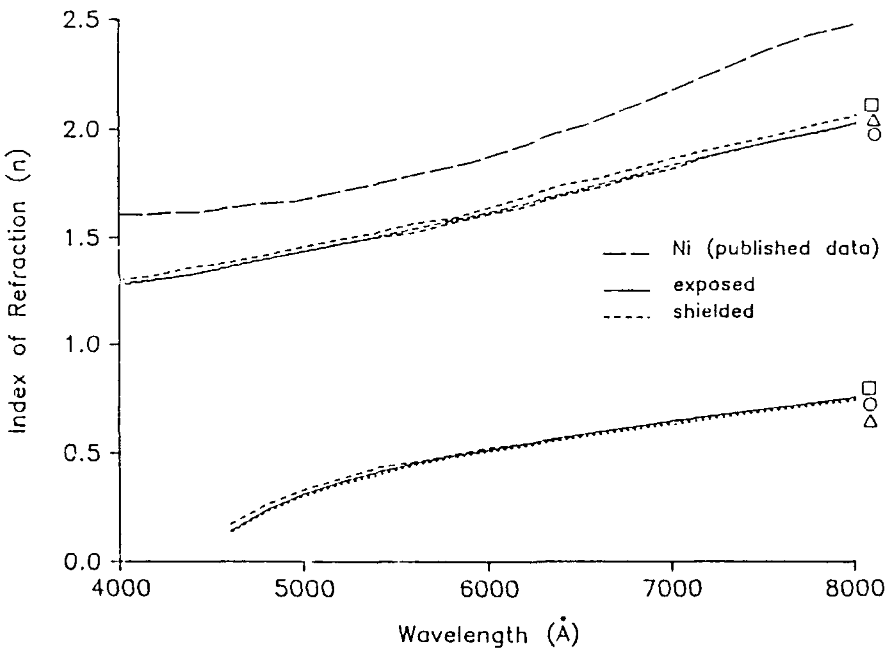

Figure 9. Index of refraction of LDEF nickel sample for exposed region and shielded region. Index of refraction of nickel (Reference 13). □ ≡ angle of incidence = $\phi = 60°$; $\Delta \equiv \phi = 70°$; $o \equiv \phi = 80°$.

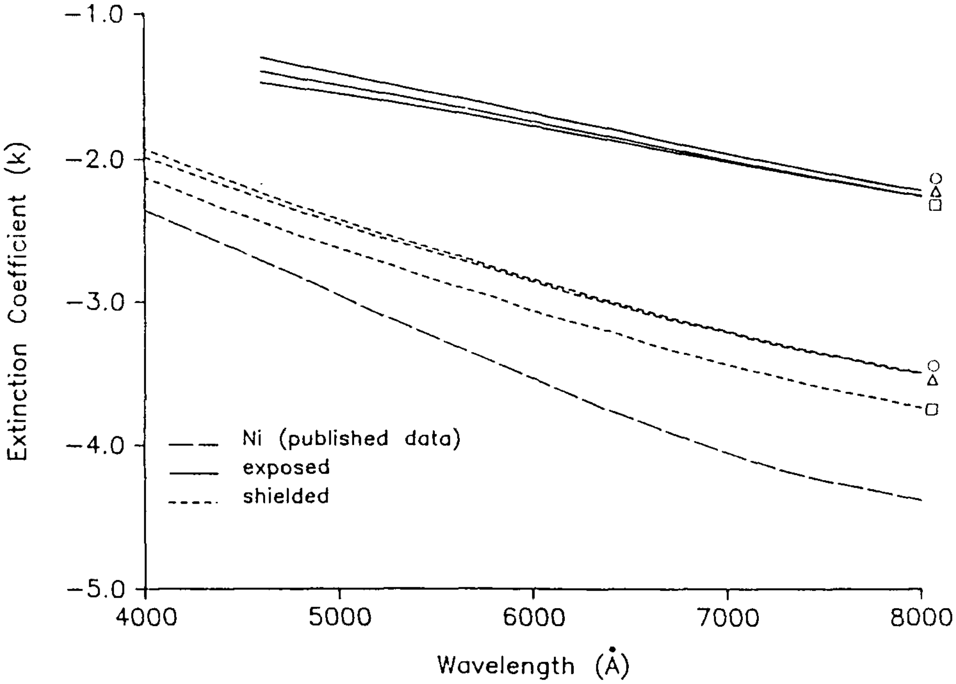

Figure 10. Extinction coefficient of LDEF nickel sample for exposed region and shielded region. Extinction coefficient of nickel (Reference 13). □ ≡ angle of incidence = ϕ = 60°; Δ ≡ ϕ = 70°; o ≡ ϕ = 80°.

Tantalum

Tantalum forms a thin layer of Ta_2O_5 when exposed to the atmosphere. The formation of the oxide is diffusion-limited as in the case of aluminum. Tantalum metal was used for the data of Weaver, et al.[15] Tantalum pentoxide is an insulator whose index of refraction does not vary by more than 1% over the visible part of the spectrum.[16] In our modelling program these small variations were ignored and assumed instead were the constant values n = 2.22 and k = 0 for the wavelength range 4000 Å to 8000 Å. The data for the exposed metal fit best to a model consisting of Ta substrate covered by a porous film of Ta_2O_5 which is 505 Å thick and contains 73% voids. The unexposed portion of the sample is covered by a 31.5 Å thick film of Ta_2O_5 free of voids. The measured optical constants of the sample are compared with the constants of the pure metal, as shown in Figures 11 and 12.

15. WEAVER, J. H., LYNCH, D. W., and OLSON, C. G. *Optical Properties of V, Ta, and Mo from 0.1 to 35 eV.* Phys. Rev., v. B10, 1974, p. 501-516.
16. BON'?IN, O. M. A., and NEAL, W. E. J. *Ellipsometric Measurements on Tantalum and Tantalum Oxide Films.* Thin Solid Films, v. 42, 1977, p. 91-96.

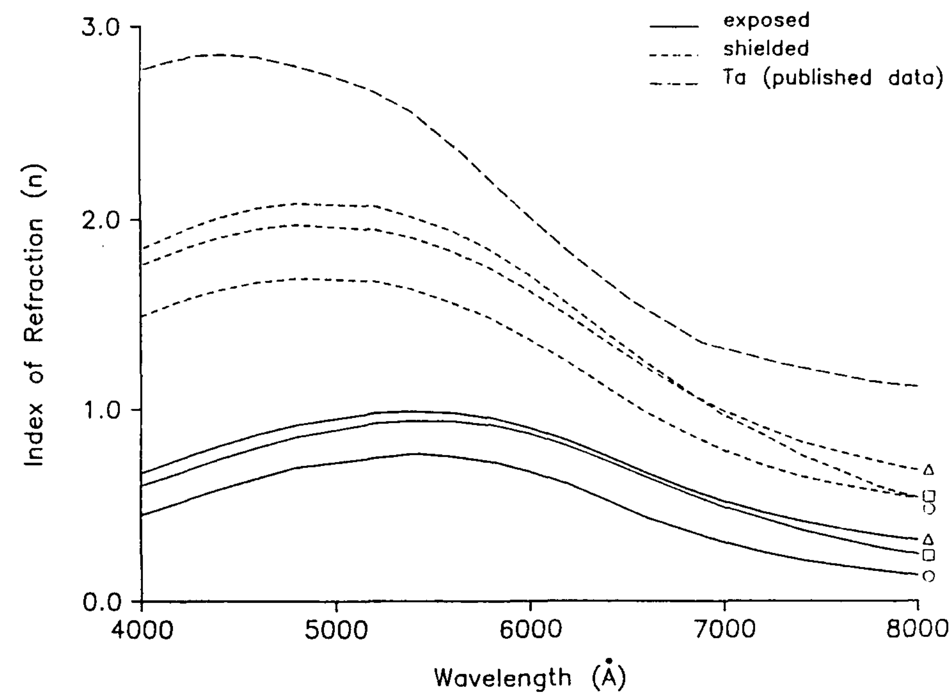

Figure 11. Index of refraction of LDEF tantalum sample for exposed region and shielded region. Index of refraction of tantalum (Reference 15). □ ≡ angle of incidence = $\phi = 60°$; $\Delta \equiv \phi = 70°$; o ≡ $\phi = 80°$.

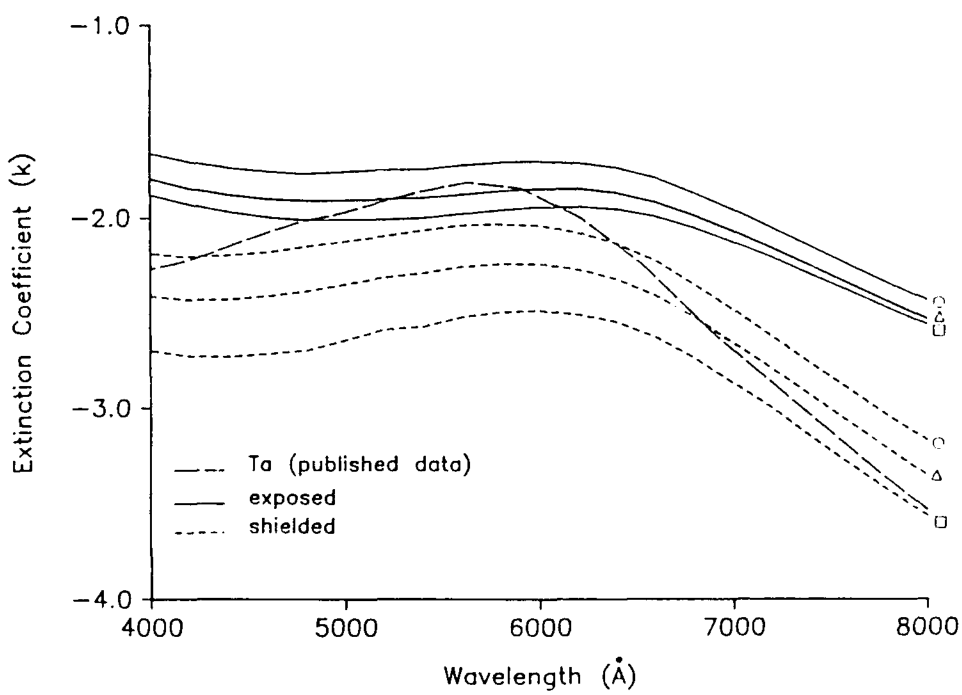

Figure 12. Extinction coefficient of LDEF tantalum sample for exposed region and shielded region. Extinction coefficient of tantalum (Reference 15). □ ≡ angle of incidence = $\phi = 60°$; $\Delta \equiv \phi = 70°$; o ≡ $\phi = 80°$.

Tungsten

The optical constants of metallic tungsten in the visible part of the spectrum have been measured by Weaver, et al.[17] Four different oxides of tungsten have been identified which contain tungsten in different oxidation states and in varying stoichiometries. In each of these compounds a tungsten atom is surrounded by an octahedron of oxygen atoms, but the compounds differ in the extent to which oxygen atoms are shared by adjacent octahedra. In addition, a compound with composition W_3O (β-tungsten) is known. The compounds have different colors which indicates a difference in their optical properties. Any reference in the literature to measurements of the optical constants of the different oxides could not be found. For that reason, the tungsten data shown in Figures 13 and 14 have not been analyzed.

Zirconium

Ellipsometry carried out in our laboratory on a freshly polished zirconium metal sample, a duplicate of the LDEF sample, revealed substantially larger values for the extinction coefficient k over the visible spectrum than older values cited in the literature.[18] For that reason, it was decided to use the measured values (listed in Table 3) in the analysis of the LDEF data.

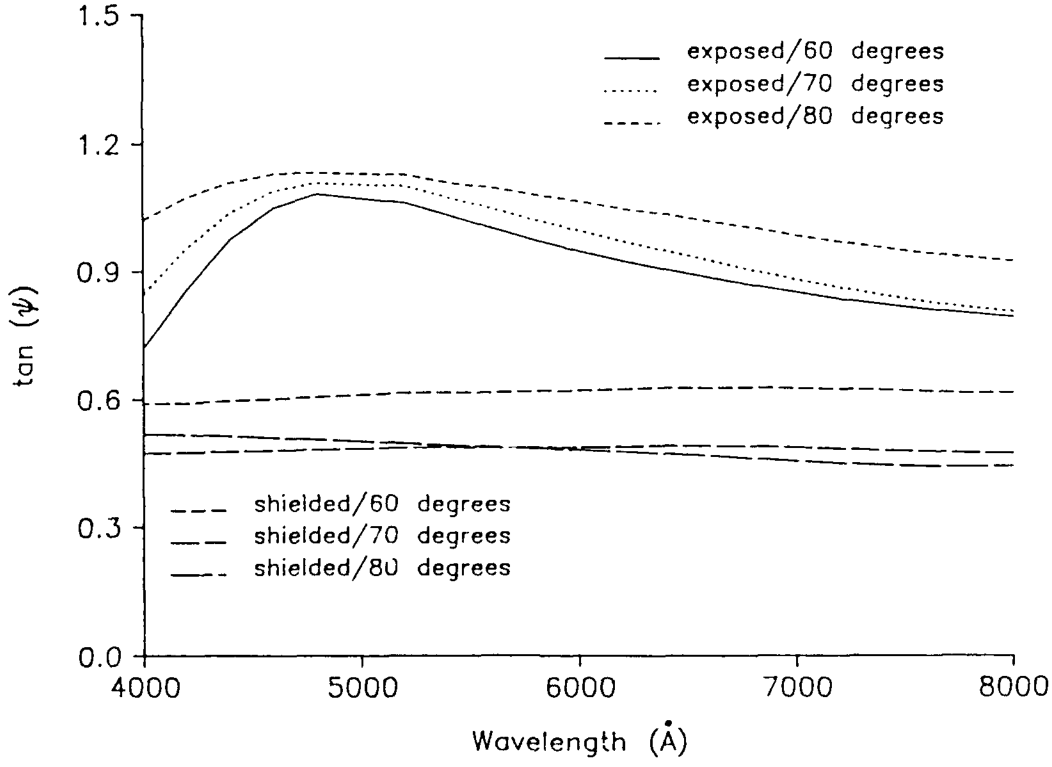

Figure 13. Tan ψ of LDEF tungsten sample for exposed region and shielded region.

17. WEAVER, J. H., OLSON, C. G., and LYNCH, D. W. *Optical Properties of Crystalline Tungsten*. Phys. Rev., v. B12, 1975, p. 1293-1297.
18. Optical Properties of Metals. Physik Daten, Fachinformationszentrum Karlsruhe, 1981, no. 18-1.

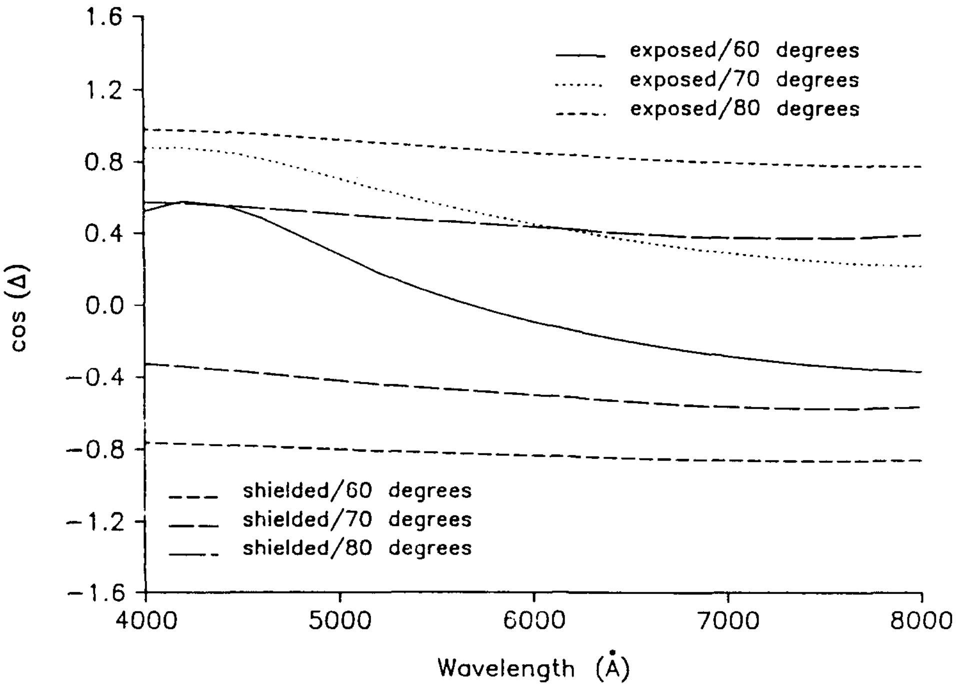

Figure 14. Cos Δ of LDEF tungsten sample for exposed region and shielded region.

Table 3. MEASURED OPTICAL CONSTANTS OFZIRCONIUM METAL

Wavelength (Å)	Index of Refraction	Extinction Coefficient
4000	1.596	2.457
4200	1.666	2.558
4400	1.743	2.657
4600	1.827	2.748
4800	1.918	2.901
5200	2.104	2.969
5400	2.192	3.021
5600	2.284	3.075
5800	2.377	3.116
6000	2.470	3.154
6200	2.558	3.168
6400	2.639	3.195
6600	2.712	3.207
6800	2.778	3.235
7000	2.832	3.252
7200	2.882	3.274
7400	2.926	3.311
7600	2.962	3.336
7800	2.999	3.360
8000	3.033	3.392

ZrO_2 is an insulator transparent to visible light. A value of its index of refraction at a single wavelength (λ = 5890 Å) is listed in Landolt-Börnstein.[19] On the assumption that ZrO_2 has negligible dispersion in the visible spectrum, it is assumed constant values n = 2.16 and k = 0 in our fitting program.

The experimental data for the exposed part of the LDEF zirconium sample are best fit by a model consisting of Zr metal covered by a 688 Å thick porous film of ZrO_2 containing 81% voids. The unexposed part of the Zr sample is covered by a film of ZrO_2 42 Å thick without voids. The data are plotted in Figures 15 and 16.

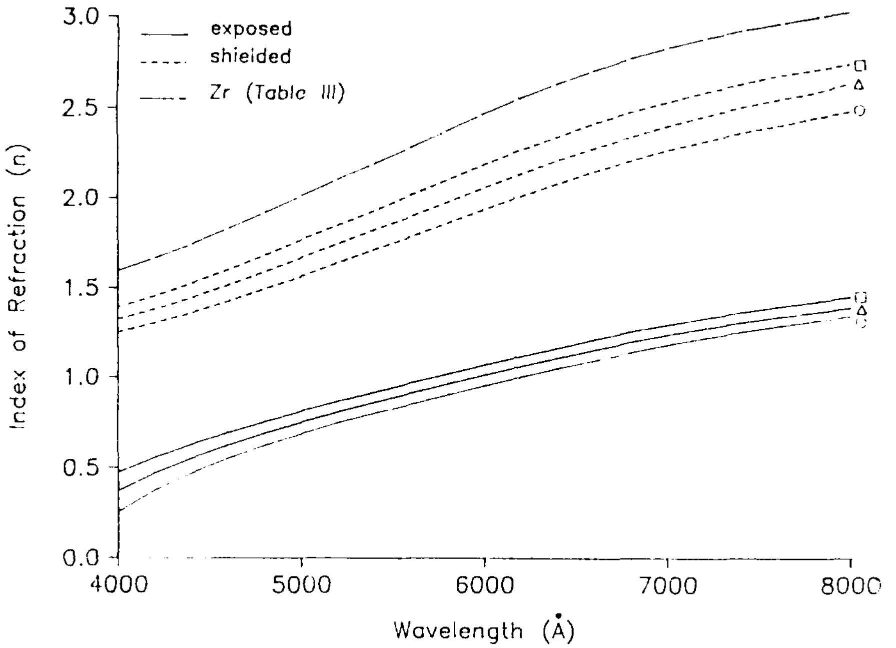

Figure 15. Index of refraction of LDEF zirconium sample for exposed region and shielded region. Index of refraction of zirconium (Table 3). □ ≡ angle of incidence = ϕ = 65°; Δ ≡ ϕ = 70°; o ≡ ϕ =75°.

CONCLUSION

A summary of the oxide thicknesses and proportion of voids as revealed by the analysis of the VASE data for both the exposed and unexposed portions of the LDEF metal samples is given in Table 4. The Ta, W, and Zr plates were mounted on tray D9, the leading edge of the LDEF and, therefore, exposed to an intense flux of atomic oxygen ($8 \times 10^{21}/cm^2$ integrated over the flight duration). According to our ellipsometric analysis, the exposed portions of the Ta and Zr samples acquired rather thick porous oxide films as a result of this exposure. In this method, the porosity of the oxide film is obtained from a least-squares fit of the ellipsometric data and will be referred to in this section as the calculated proportion of voids. All of the LDEF metal samples were also examined with an optical metallograph which employs a different technique of determining film porosity and yields a value for the *measured porosity* of the metal samples. The latter technique relies upon the difference in

19. LANDOLT-BÖRNSTEIN. Zahlenwerte und Funktionen, v. II, part 8, 1962, p. 2-151.

contrast in the field of view at 500X, whereby dark regions are interpreted as voids and light areas as those containing the metal substrate. A computer program is used to determine an average percentage of voids using at least 10 different sampling spots on the specimen to ensure adequate representation of the whole surface.

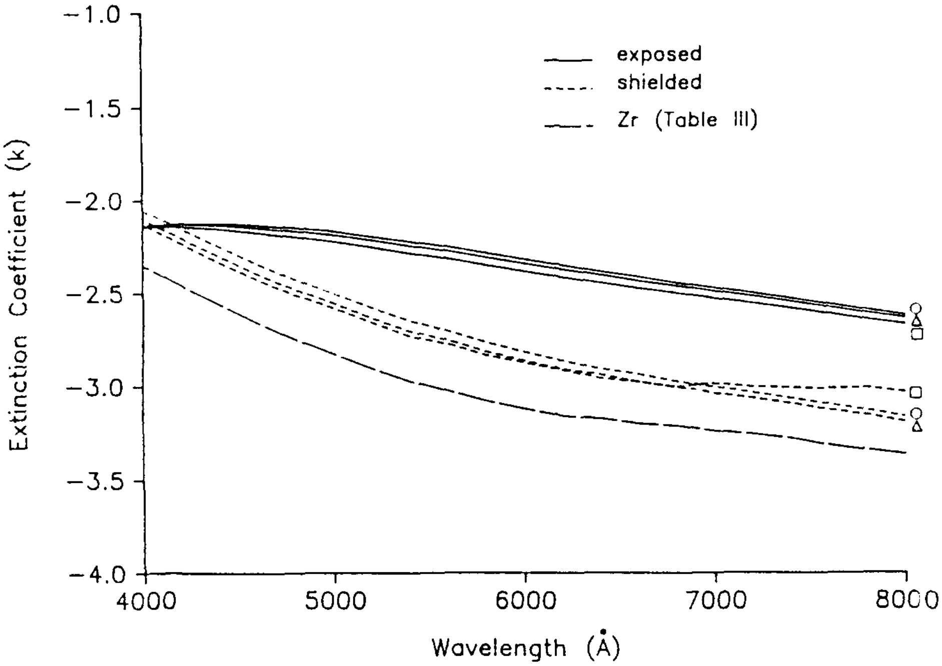

Figure 16. Extinction coefficient of LDEF zirconium sample for exposed region and shielded region. Extinction coefficient of zirconium (Table 3). □ ≡ angle of incidence = ϕ = 65°; Δ ≡ ϕ = 70°; o ≡ ϕ = 75°.

Table 4. SUMMARY OF RESULTS

Sample	Exposed (E) or Shielded (S)	Oxide	Thickness of Oxide	Proportion of Voids
Al	E	Al_2O_3	395	0
Al	S	Al_2O_3	68	0
Cu	E	Cu_2O	1039	0.71
Cu	S	Cu_2O	449	0.69
Ni	E	NiO	687	0.65
Ni	S	NiO	60	0
Ta	E	Ta_2O_5	505	0.73
Ta	S	Ta_2O_5	31.5	0
W	E	?	not known	not known
W	S	?	not known	not known
Zr	E	ZrO_2	688	0.81
Zr	S	ZrO_2	42	0

The calculated proportion of voids in the Zr sample (0.81) corresponded well with the measured porosity (0.69). However, for exposed Ta the calculated proportion of voids (0.73) was much larger than the measured porosity (0.10), possibly because the pores formed in the Ta_2O_5 film are too small to be resolved with an optical microscope.

The Al and Ni plates were mounted on tray D3, on the trailing edge of the LDEF and, therefore, exposed to an integrated oxygen flux (4 x $10^3/cm^2$) less than for any other placement on the satellite. Nevertheless, according to our ellipsometric analysis, thick oxide films were formed on the exposed portions of both metals, porous in the case of Ni (calculated void proportion, 0.65; measured porosity, 0.29), but practically free of voids for Al (for both calculated void proportion and measured porosity). Because the calculated number of oxygen atoms in such a film is much greater (on the order of 10^{17} atoms/cm^2) than the integrated flux of oxygen atoms, some other mechanism of oxide formation is suspected. For the Zr, Ta, Al, and Ni samples the shielded portions of the plates are covered by relatively thin non-porous oxide films typical of exposure to air at atmospheric pressure.

The most puzzling results were obtained for the Cu sample, mounted on the earth end of the satellite (tray G12, oxygen flux 5 x $10^{19}/cm^2$) because of very thick porous Cu_2O films on the exposed portion (0.71 calculated proportion of voids, 0.76 measured porosity), as well as on the shielded portion (0.69 calculated voids, 0.45 measured porosity). Micrographs of both regions show many scratches on the surface, probably as a result of careless handling, that might cause the ellipsometric analysis to be unreliable.

The extent to which the metal samples were subject to contamination from sources other than atomic oxygen; for example, due to ablation of paint and other materials from LDEF structure, is a subject of speculation. There is some evidence of cross-contamination during flight that, if extensive, could affect the outcome of the ellipsometric analysis. However, the mean square error, which is a measure of goodness of fit between the model and the experimental data, is quite small for the analysis of the Al, Ni, and Zr samples (less than 5%). This is a strong indication that the model is correct in these cases. However, for the analysis of the Ta and Cu samples, the mean square error is rather high, which suggests that a different model might provide a more accurate representation of the surface layer. A discussion of the reasons for the high porosity of most of the oxide films, and an explanation of the absence of porosity in the case of the Al_2O_3 film, is beyond the scope of the study reported here.

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Wolfgang Franzen, Judith S. Brodkin, Louise C. Sengupta and Paul L. Sagalyn

Technical Report MTL TR 92-2, February 1992, 19 pp-illus-tables, D/A Project: A1205.AH84

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